Supplementary Information for “Nanoelectrodes Reveal Electrochemistry of Single Nickelhydroxide Nanoparticles”

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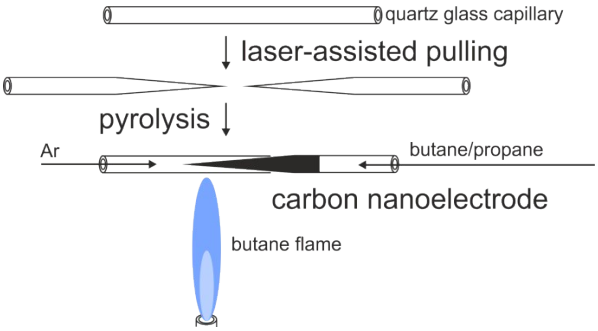
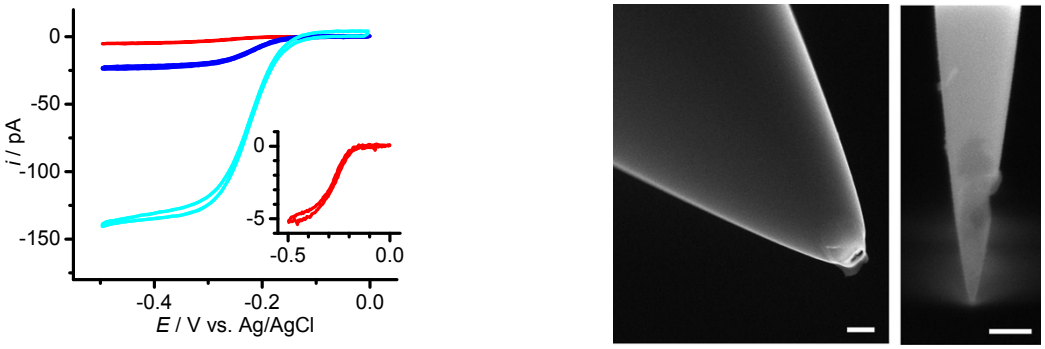
Electrode fabrication and characterization



Supporting Figure 1. Fabrication of carbon nanoelectrodes by laser-assisted pulling of quartz glass capillaries and subsequent pyrolysis of butane/propane gas in inert argon atmosphere.

Quartz glass capillaries with an inner diameter of 0.9 mm and an outer diameter of 1.2 mm (*Sutter Instruments*) were pulled to nanopipettes using a P-2000 laser puller (*Sutter Instruments*) with a typical set of parameters: Heat 750, Filament 4, Velocity 45, Delay 130 and Pull 120. The nanopipettes were filled with a 80:20 butane/propane mixture (*Campingaz*) using Tygon tubing and inserted into an non-pulled capillary of the same specifications which was connected to an Ar cylinder with a slight Ar flow. Using a butane jet flame, the nanopipette was heated to approx. 1300 °C for several seconds until the black conductive carbon had deposited. Carbon nanoelectrodes were contacted by inserting a copper wire and used without further treatment.

a **b**



Supporting Figure 2. Characterization of carbon nanoelectrodes. Cyclic voltammograms in 5 mM $[Ru(NH_3)_6]Cl_3$, 0.1 M KCl for selected electrodes with radii of 2, 11, and 68 nm (a). Inset: Enlargement of the CV for the smallest electrode. SEM images of different electrodes from different angles (b). Electrochemically estimated radii were 60 nm (left electrode) and 4 nm (right electrode). Scale bars 200 nm.

General Electrochemistry

All reagents were of analytic grade. All measurements were performed either using a Modulab potentiostat (*Solartron Analytical*) equipped with a femtoammeter module, a VA-10 voltammetric amplifier (*npi*) or a L/M-EPC 7B patch-clamp amplifier (*List Medical*) in two-electrode configuration with a Ag/AgCl/3 M KCl counter-reference electrode. The quality and size of carbon nanoelectrodes was tested by cyclic voltammograms in 5 mM $[Ru(NH_3)_3]Cl_3$, 0.1 M KCl. According to the equation I_{ss}=4.64nFcrD used to describe the current limited by partially spherical diffusion of electroactive species to a disk-shaped nanoelectrode[1] the apparent electrode radius was estimated. $Ni(OH)_2$ was deposited cathodically from 5 mM $NiCl_2$ by applying -1 V vs. Ag/AgCl/3 M KCl for varying electrolysis times. However, at the nanometric electrodes only poor correlation between the electrolysis time and the amount of deposited $Ni(OH)_2$ was observed. CVs for the OER were performed in 0.1 M KOH at 10 mV/s. Before the analysis of peak currents as a function of the scan rate in 0.1 M KOH the electrodes were cycled for at least 500 cycles in the same solution in a potential range between 0 and 0.8 V vs. Ag/AgCl/3 M KCl. The CVs shown in figure 2 are smoothed using an adjacent-averaging filter with a width of 5 data points. However, the peak analysis was done before smoothing by taking the average peak intensities from 3 adjacent cycles.

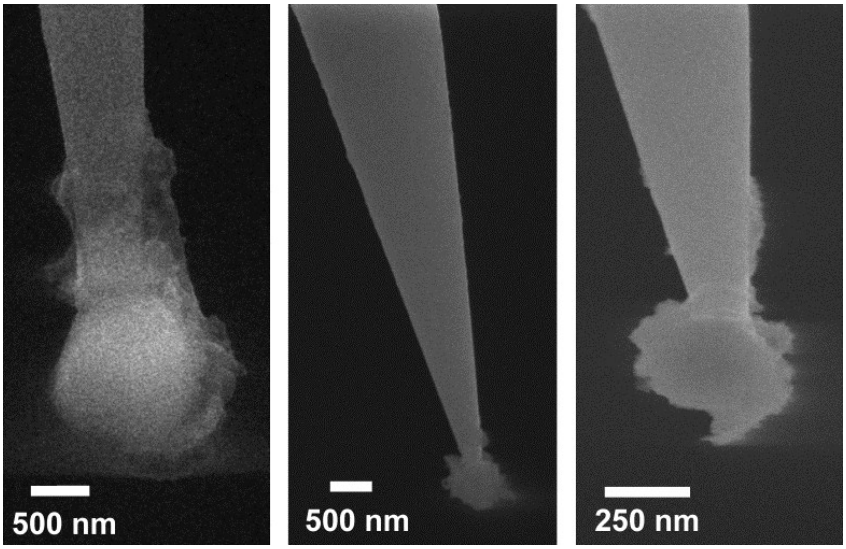
Estimation of particle size and turnover frequency

Particle sizes were estimated from the charge transferred during the anodic peak for the oxidation of $Ni(OH)_2$ (Figure 3a, inset) according to Faraday’s law of electrolysis $n = q/zF$. The charge is proportional to the amount of deposited catalyst material and thus

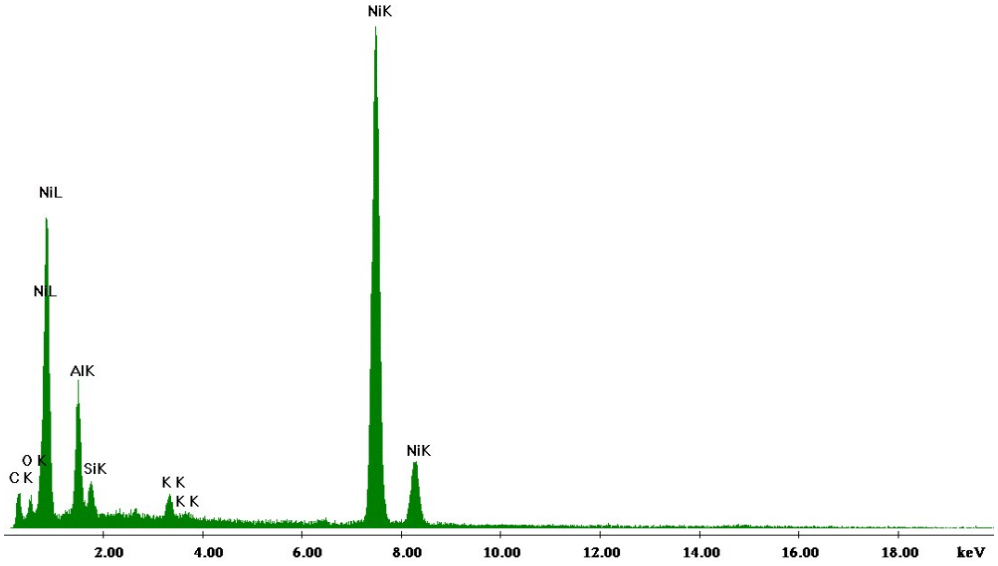
the volume of individual $Ni(OH)_2$ particles assuming a density of 4.1 g cm^{-3}. [2] From the particle volume, assuming spherical particle geometry, particle radii and surface areas were calculated. The electrochemically estimated particle sizes were in good agreement with particle sizes determined from SEM images. For instance, the electrochemical particle sizes for the two particles shown in figure 1 were 227 nm and 55 nm. Only those electrodes for which the calculated particle size was larger than the initial carbon electrode radius were used for further analysis. Turnover frequencies were computed according to $TOF = i_{OER}/4Fn_{Ni}$, with i_{OER} the OER current extracted from the steady-state voltammograms at a potential of 1.88 vs. RHE and n_{Ni} the amount of deposited $Ni(OH)_2$.

SEM/EDX characterisation of carbon nanoelectrodes

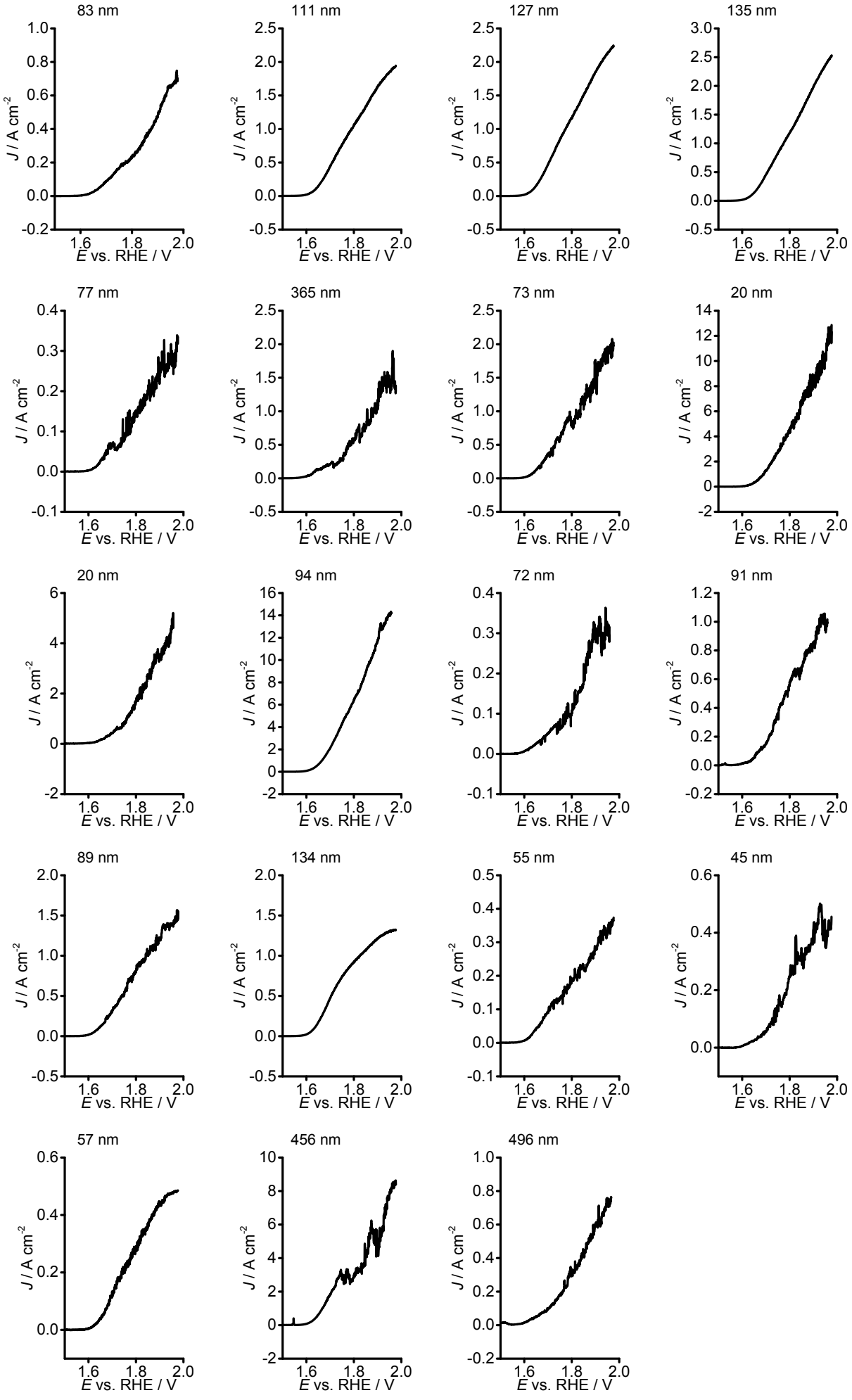
SEM imaging and energy-dispersive X-ray analysis of nanoelectrodes were conducted using an EM Quanta 3 D FEG electron microscope (*FEI*).



Supporting Figure 3. Additional SEM images of $Ni(OH)_2$ particles on carbon nanoelectrodes. The electrochemically estimated radii were 446, 186 and 160 nm from left to right.



Supporting Figure 4. EDX analysis of a single $Ni(OH)_2$ (r = 1 µm) particle on a quartz-surrounded carbon electrode showing the expected characteristic lines for nickel, silicium, oxygen, carbon as well as potassium from residues of the electrolyte solution and aluminum from the sample holder.



Supporting Figure 5. Polarization curves for the OER in 0.1 M KOH. Corresponding particle radii are indicated above the graphs.

References

1 P. Actis, S. Tokar, J. Clausmeyer, B. Babakinejad, S. Mikhaleva, R. Cornut, Y. Takahashi, A. López Córdoba, P. Novak, A. I. Shevchuck, J. A. Dougan, S. G. Kazarian, P. V. Gorelkin, A. S. Erofeev, I. V. Yaminsky, P. R. Unwin, W. Schuhmann, D. Klenerman, D. A. Rusakov, E. V. Sviderskaya and Y. E. Korchev, *ACS Nano*, 2014, **8**, 875; C. Lefrou and R. Cornut, *ChemPhysChem*, 2010, **11**, 547.

2 D. Cibrev, M. Jankulovska, T. Lana-Villarreal and R. Gómez, *Int. J. Hydrogen Energy*, 2013, **38**, 2746; Y.-G. Zhou, N. V. Rees and R. G. Compton, *Angew. Chem. Int. Ed.*, 2011, **50**, 4219.